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Combined *in situ* X-ray absorption and diffuse reflectance infrared spectroscopy: An attractive tool for catalytic investigations

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ABSTRACT

Catalysis investigations are often followed in a range of spectroscopic techniques. While diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be done on a bench-top instrument, X-ray absorption spectroscopy (XAS) techniques, such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) require synchrotron light. In order to ensure the same conditions during *in situ* catalysis for each method, a combined XAS/DRIFTS has been developed at beamline X18A at the National Synchrotron Light Source, Brookhaven National Laboratory. A rapid-scan FTIR spectrometer capable of both mid- and far-infrared measurements is equipped with an arm to redirect the IR beam outside the spectrometer. An *in situ* reaction chamber, equipped with glassy carbon windows for X-ray light and a KBr window for IR light passage is installed firmly on the arm. The reaction cell can be heated to 600 °C and allows passage of gases through the catalyst so that both XAS and DRIFTS techniques can be done simultaneously in controlled environment conditions. Together with a fast-moving monochromator for quick-EXAFS and mass-spectrometric residual gas analysis, this new tool is a powerful method for testing catalytic reactions in real time.

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1. Introduction

Many physical and chemical reactions need to be studied *in situ* in order to follow the reaction pathways and understand the mechanisms of transformations. A complete picture of many catalytic processes can only be obtained by combining data from several complementary techniques. However, merging data from independent experiments can be challenging, particularly when the reaction is sensitive to the changes in external factors, e.g., temperature, gas environment, etc. Thus, there is a need to combine a number of techniques simultaneously, probing the catalytic surface *in situ* under an identical set of conditions.

X-ray absorption spectroscopy (XAS) techniques, namely EXAFS and XANES, investigate the catalyst structure and electronic state and monitor their changes during the reaction. However, they are inefficient for studies of adsorbates and ligands attached to the catalyst surface during an *in situ* catalytic reaction. This difficulty could be alleviated using vibrational techniques, e.g., Raman and infrared spectroscopies. Of IR techniques, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is particularly useful because it studies powder surfaces and provides penetration depths larger than, for instance, that of attenuated total reflection. Transmission IR

usually requires a pressed wafer for the measurement, which limits its usefulness for *in situ* catalysis investigation because of diffusion problems, although there are approaches, in which the catalyst is sprayed onto a mesh or window [1,2]. In addition to the gas phase characterization, the technique analyses species adsorbed on the surface of the catalyst (e.g. chemical structure of the active centers and reaction intermediates) can be used even if the sample is opaque for transmission IR measurements [3]. Several authors have emphasized the power DRIFTS and XAS studies for the characterization of catalytic surfaces [4,5]. They were recently integrated successfully with X-ray methods for *in situ* investigations, providing a unique opportunity to understand the interactions of catalysts and reactants [6–8]. In this work we present a new instrument for the combined use of X-ray absorption spectroscopy and infrared spectroscopy techniques complemented by mass-spectrometric residual gas analysis (RGA) for the *in situ* studies of nanocatalysts. These instruments provide access to a broad energy range in both X-ray and IR regimes as well as a wide temperature range. The new setup was installed and tested at beamline X18A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory in Upton, NY, USA.

2. Design and setup

Beamline X18A is a bending magnet line, which uses a home-built Si(1 1 1) channel-cut monochromator and a rhodium-coated

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toroidal focusing mirror to provide a ~ 1.0 mm (horizontal) \times 0.5 mm (vertical) spot size with a flux of $\sim 2.5 \times 10^{11}$ photons/s at 10 keV. The monochromator is capable of quick-scanning (QEXAFS) in a manner similar to one previously described [9]. Currently, an XAS scan can be completed in 0.5 s with 1000 equally spaced data points, so that either XANES or a full EXAFS scan with acceptable resolution and quality are obtained. Such conditions are satisfactory for concentrated samples that are measured in transmission, among those metal catalysts with a few weight percent loading on the support made of aluminum, silicon and other light element oxides [10].

The instrument for collecting combined XAS and DRIFTS data consists of the IR spectrometer and a specially prototyped external DRIFTS accessory, Fig. 1. The infrared spectrometer, a Thermo-Nicolet 6700, [11] is equipped with two beamsplitters (KBr and solid substrate) and a range of detectors for scanning in both mid- and far-IR modes. In the rapid-scanning mode a good quality DRIFTS spectrum can be collected in about 10 s. The DRIFTS setup consists of a DaVinci arm [12] firmly attached to a Praying Mantis DRIFTS accessory [13] and a high-temperature reaction chamber [14]. All accessories were specially modified to re-image the infrared beam outside the spectrometer, in order to accommodate the X-ray beam path through the reaction chamber. To precisely align the spectrometer and the XAS/DRIFTS accessory to the X-ray beam, the entire DRIFTS setup is mounted on a custom-made table with five independent, computer-controlled motors. Three motors lift and tilt the table vertically, one motor adjusts the horizontal position perpendicular to the beam, and another motor rotates the table about a vertical axis through the sample position. The entire optical path of the XAS/DRIFTS instrument is purged with dry nitrogen to remove traces of water vapor and carbon dioxide, which would otherwise mask a large portion of the IR spectrum. Three gas-filled ion chambers, positioned one before and two after the reaction chamber, measure the intensity of the X-ray beam. A reference sample (e.g. a metal foil), positioned downstream of the transmission detector, is used for X-ray energy calibration. Fig. 2 shows the interior of the X18A hutch with the XAS/DRIFTS setup on its custom-made table, together with X-ray ion chambers, reactor gas tubes and water cooling tubes.

Fig. 3 shows a sketch of the sample cell. The cell allows the reaction gas to either blanket the sample powder or to flow through it with a maximum pressure of about 1.3 atm. The sample can be heated to 600 °C, while the body of the chamber is cooled with water to protect the IR windows [14]. The sample cup of the

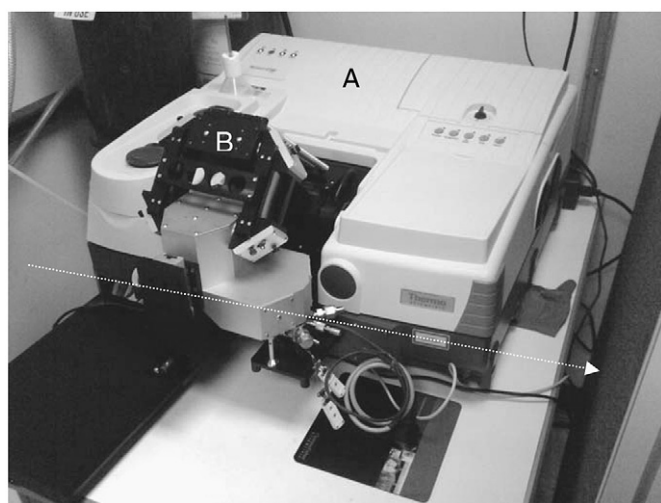


Fig. 1. (A) Nicolet 6700 IR spectrometer with (B) assembled Harrick DRIFTS attachment. The X-ray beam passes as indicated by the arrow.

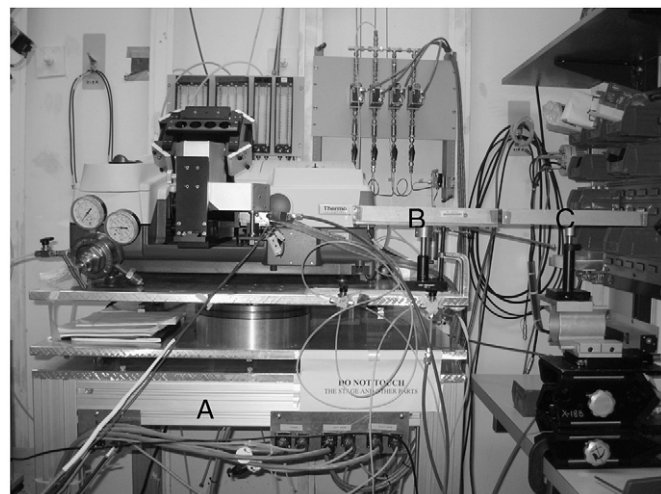


Fig. 2. XAS/DRIFTS setup situated in the X18A hutch, showing the positioning table underneath the spectrometer (A) and two ion chambers, for measuring transmitted X-ray intensity, I_t and for energy calibration, I_{ref} (B and C, respectively) with a metal foil between them.

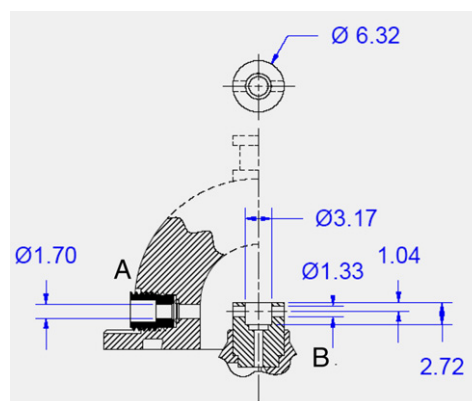


Fig. 3. Cross-section of the XAS/DRIFTS reactor dome with dimensions; X-ray beam passes through (A) a glassy carbon window and (B) an opening in the sample cup.

reaction chamber has an inner diameter of 3.17 mm and the total loading of the sample is about 20 mg. The entrance and exit X-ray windows, drilled in the reaction chamber dome, are made of 1.7 mm diameter glassy carbon. The X-ray beam traverses through two circular openings in the sample cup with a center of 1.04 mm below the top surface that is probed by the IR light. The closest distance from the top surface to the top of the circular opening (the X-ray path) is 0.37 mm. We have designed a set of removable inserts with smaller diameters for studying samples with lower Z numbers, for which X-ray absorption length is smaller. Since the penetration depth of infrared radiation into the sample can reach 3 mm when using non-absorbing diluting powders (e.g. KBr or Al_2O_3) in the IR-transparent regions [15], a significant portion of the IR beam samples the same volume through which the X-ray beam traverses. The internal dead volume of the cell is about 14 mL. The largest purge rate of our mass flow controllers is 50 mL/min, allowing the gas in the cell to be replaced in about 17 s.

Reaction and product gases are fed into a custom-made residual gas analyzer (RGA) that contains a quadrupole mass spectrometer with a mass range up to 200 amu (Stanford Research Systems [16]). A multiport valve allows the on-line analysis of either the feed or product. The input gas splits so that only a fraction of the total gas flow goes into the RGA through a capillary (50 μm inner diameter and 1 m long). With the above gas flow rate and by minimizing the

distance between the reactor and the RGA, its response time is about 20 s [17].

We have extensively tested the new setup in both *ex situ* and *in situ* regimes. To summarize the results of testing, we found that the setup can be used with X-ray energies from 8 to 22 keV without a loss of sensitivity, and the DRIFTS can successfully probe the catalyst surface, as observed through CO adsorption on supported Pt nanoparticles on Al₂O₃. These results will be presented elsewhere [18].

3. Conclusion

The combination of infrared and X-ray absorption spectroscopies in a single experiment provides a fast and reliable analytic method for solving structural and kinetic problems of interest to catalytic science. New research capabilities are described here that employ a versatile instrument for *in situ* investigation of a broad range of metals by complementary absorption and vibrational spectroscopies for catalysis research. Due to the QEXAFS capability of the beamline and the fast-response of the IR detectors and gas analysis system, combined X-ray and IR spectroscopy data collection in tens of seconds range under *in situ* conditions are now possible at NSLS beamline X18A.

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